metal-organic papers

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Peter D. W. Boyd* and C. E. F. Rickard

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Correspondence e-mail: pdw.boyd@auckland.ac.nz

Key indicators

Single-crystal X-ray study T = 203 KMean σ (C–C) = 0.003 Å R factor = 0.026 wR factor = 0.072 Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

[*µ*-*N*,*N*'-Bis(3-aminopropyl)oxamidato(2–)]bis[(2,2'-bipyridine)copper(II)] dinitrate

The title compound, $[Cu_2(C_8H_{16}N_4O_2)(C_{10}H_8N_2)_2](NO_3)_2$, contains a centrosymmetric binuclear copper(II) complex bridged by a deprotonated oxamide ligand. The Cu atoms have a distorted square-pyramidal coordination geometry, with one of the 2,2'-bipyridine N atoms at the apex. The copper complex cations assemble in chains along the *c* axis *via* π - π overlaps of bipyridine ligands of neighbouring complexes. These chains are connected in the crystal structure *via* N-H···O and C-H···O hydrogen bonds with the nitrate ions.

Comment

The oxamidate dianion is a versatile bridging ligand used in the design and synthesis of polymetallic complexes (Ojima & Nonoyama, 1988; Ruiz *et al.*, 1999). A large variety of homoand heterobinuclear complexes of multidentate ligands based on functionalized oxamides have been reported. The title complex, (I), was prepared by Ojima & Nonoyama (1972) from a reaction of N,N'-bis(3-aminopropyl)oxamidatocopper(II), Cu(apoxd), with mono(2,2'-bipyridine)copper(II) nitrate, [Cu(bipy)](NO₃)₂, in alkaline solution, and was characterized by magnetic and spectroscopic measurements.



The molecular structure of (I), $[Cu_2(apoxd)(bipy)_2](NO_3)_2$, is shown in Fig. 1. The complex cation, $[Cu_2(apoxd)-(bipy)_2]^{2+}$, is a centrosymmetric dimer. Two five-coordinate Cu^{II} ions are bridged by the deprotonated oxamide group of the *N*,*N'*-bis(3-aminopropyl)oxamide ligand in a *trans* conformation, with $Cu \cdots Cu = 5.2504$ (4) Å. Each five-coordinate Cu^{II} ion has a near square-pyramidal geometry, with a longer contact to atom O2 [3.115 (3) Å] of the nitrate anion from beneath the basal plane of the coordination pyramid (Table 1). Atoms N2 and O1 of the bridging oxamidate anion occupy adjacent positions on the base of the pyramid along with atoms N1 and N3. Atom N4 of the 2,2'-bipyridine ligand is at the apex of the pyramid, with the Cu—N4 distance significantly longer than the basal Cu—N3 distance, indicative

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7305 measured reflections

 $\begin{array}{l} R_{\rm int} = 0.015 \\ \theta_{\rm max} = 27.5^{\circ} \end{array}$

3353 independent reflections

3123 reflections with $I > 2\sigma(I)$



Figure 1

The molecular structure of (I), showing the atom-numbering scheme, with 50% probability displacement ellipsoids. H atoms are shown as arbitrary spheres. The dashed line indicates a hydrogen bond. (Symmetry code for unlabelled atoms: -x, 1 - y, -z.)



Figure 2

The packing arrangement of complex (I), viewed along the *a* axis, showing the π - π stacking between complex cations. H atoms have been omitted.

of a Jahn–Teller distorted geometry. The 12-atom plane of the 2,2'-bipyridine ligand (C5–C14/N3/N4, r.m.s. deviation 0.05 Å) makes an angle of 88.10 (4)° to the Cu/O1/N1/N2/N3 basal plane (r.m.s. deviation 0.252 Å). The overall molecular geometry of the [Cu₂(apoxd)(bipy)₂]²⁺ cation is very similar to an analogous [Cu₂(apoxd)(pyrimidine)₂]²⁺ complex cation (Dominguez-Vera *et al.*, 1998) and a related [Cu₂(aeoxd)(diazafluorenone)₂]²⁺ complex (Li *et al.*, 2005).

The ions of (I) assemble in the crystal structure as shown in Fig. 2. The dimeric units form chains along the *c* axis *via* π - π stacking of the 2,2'-bipyridine ligands with those of adjacent complexes (interplanar distance 3.459 Å). The O atoms of the nitrate ion form hydrogen bonds to H atoms on the primary amine atom N1, the methylene C atoms C1 and C3, and bipyridine C atoms C7 and C8 (Table 2). These connect each of the [Cu₂(apoxd)(bipy)₂]²⁺ cation chains within the crystal structure.

Experimental

Complex (I) was prepared and crystallized as described by Ojima & Nonoyama (1972).

Crystal data

 $[Cu_2(C_8H_{16}N_4O_2)(C_{10}H_8N_2)_2]$ - $\nu = 112.436 \ (1)^{\circ}$ V = 769.31 (5) Å³ $(NO_3)_2$ $M_r = 763.72$ Z = 1Triclinic, $P\overline{1}$ $D_x = 1.648 \text{ Mg m}^{-3}$ a = 8.9069 (3) Å Mo $K\alpha$ radiation b = 10.3003 (4) Å $\mu = 1.45 \text{ mm}^$ c = 10.3457 (4) Å T = 203 (2) K $\alpha = 103.290 (1)^{\circ}$ Prism, green $\beta = 107.605(1)^{\circ}$ $0.20 \times 0.18 \times 0.15 \text{ mm}$ Data collection

Siemens SMART CCD areadetector diffractometer ω scans Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\min} = 0.760, T_{\max} = 0.812$

Refinement

ł

3

F

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	+ 0.358P]
$VR(F^2) = 0.072$	where $P = (F_0^2 + 2F_c^2)/3$
f = 1.06	$(\Delta/\sigma)_{\rm max} < 0.001$
353 reflections	$\Delta \rho_{\rm max} = 0.62 \ {\rm e} \ {\rm \AA}^{-3}$
17 parameters	$\Delta \rho_{\rm min} = -0.50 \text{ e} \text{ Å}^{-3}$
I-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu-N2	1.9468 (13)	Cu-N3	2.0173 (14)
Cu-O1 ⁱ	2.0126 (12)	Cu-N4	2.2276 (15)
Cu-N1	2.0166 (14)		
N2-Cu-O1 ⁱ	83.86 (5)	N1-Cu-N3	91.03 (6)
N2-Cu-N1	92.71 (6)	O1 ⁱ -Cu-N4	104.96 (5)
D1 ⁱ -Cu-N1	149.59 (6)	N1-Cu-N4	105.21 (6)
N2-Cu-N3	175.79 (5)	N3-Cu-N4	77.33 (6)
D1 ⁱ -Cu-N3	91.94 (5)		

Symmetry code: (i) -x, -y + 1, -z.

Table 2	
Hydrogen-bond	geon

		•	
Hydrogen-bond	geometry	(A,	°).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$N1-H1A\cdots O2$	0.91	2.21	2.928 (2)	135
$N1 - H1A \cdots O2^{ii}$	0.91	2.63	3.080 (2)	111
$N1 - H1D \cdots O4^{ii}$	0.91	2.16	3.032 (2)	161
$C1 - H1B \cdots O4^{iii}$	0.98	2.53	3.413 (3)	150
$C3-H3B\cdots O4^{iii}$	0.98	2.68	3.528 (2)	145
$C7-H7A\cdots O4^{iv}$	0.94	2.45	3.348 (2)	160
$C8 - H8A \cdots O3^{iv}$	0.94	2.65	3.253 (3)	122

Symmetry codes: (ii) -x, -y + 1, -z + 1; (iii) x + 1, y, z; (iv) x, y - 1, z.

H atoms were placed in calculated positions and refined using a riding model, with C–H = 0.93–0.98 Å and N–H = 0.91 Å, and with $U_{\rm iso}({\rm H}) = 1.2 U_{\rm eq}({\rm C,N})$ for methylene and amine H atoms, or $1.5 U_{\rm eq}({\rm C})$ for aromatic C atoms in the bipyridine group.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Macrae *et*

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al., 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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